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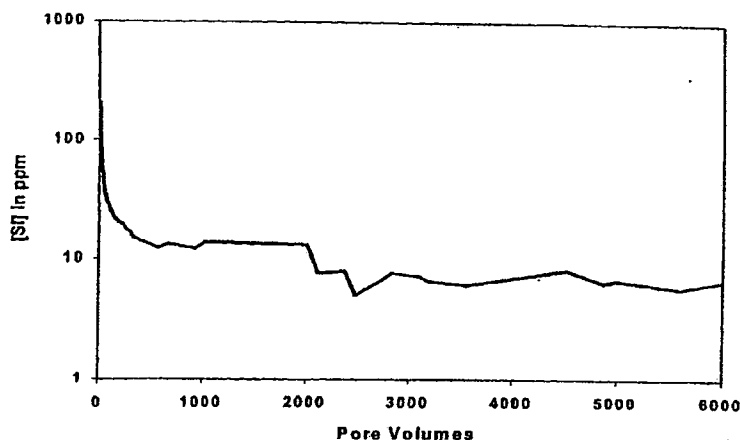
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(54) Title: MICROCAPSULE WELL TREATMENT

Scale Inhibitor Release Profile from a Plastic Capsule



(57) Abstract: A material and a device for releasing chemicals in a fluid environment is disclosed, and a method for releasing substances into downhole fluid environments. The invention also relates to materials for sand control and hydraulic fracturing. The substance release device typically comprises a polymeric material for releasing a substance into a downhole fluid environment in a well, and in preferred embodiments the material comprises a spherical, plastic chemical release capsule which is hard, permeable and may encapsulate a range of solids and/or liquids for subsequent release. These solids or liquids can include inhibitors such as scale inhibitors and other oilfield production chemicals for release into the wellbore of an oil or gas producing well or a water injection well.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

## microcapsule well treatment

1  
2  
3 This invention relates to material for releasing  
4 chemicals in a fluid environment, and to a method of  
5 producing the material. In particular, this invention  
6 relates to materials for sand control and hydraulic  
7 fracturing, the same materials releasing chemicals in  
8 a fluid environment, and to a method of producing  
9 these materials.  
10  
11 Advances in drilling and completion technology have  
12 revolutionised new field development and in-fill  
13 drilling strategies. The use of subsea and/or  
14 horizontal well completions is now common and in some  
15 cases these complex wells require sand control  
16 measures to be installed to maintain the integrity of  
17 the wellbore and prevent it collapsing. A variety of  
18 well completions are conventionally used for sand  
19 control purposes including fracture packing and  
20 gravel-packing techniques, prep-packed screens, wire

1 wrapped screens and expandable screens. It is  
2 preferred that the flow of fluids through the sand  
3 control system is not impaired since this can reduce  
4 the productivity and/or injectivity of the well.  
5 Hydraulic fracturing is used to improve well  
6 productivity. It is therefore preferred that the flow  
7 of fluids into and through the propped fracture is  
8 not impaired since this can also reduce the  
9 productivity and/or injectivity of the well.

10

11 The installation of subsea and/or horizontal well  
12 completions also increase the complexity, logistical  
13 difficulty and cost of intervention for the  
14 mitigation of production chemistry problems such as  
15 inorganic scale formation, asphaltene and wax  
16 deposition, corrosion and bacterial growth on the  
17 wellbore conduits.

18

19 According to the present invention there is provided  
20 a substance release device comprising a polymeric  
21 material for releasing a substance into a downhole  
22 fluid environment in a well.

23

24 In preferred embodiments the material comprises a  
25 spherical, plastic chemical release capsule which is  
26 hard, permeable and may encapsulate a range of solids  
27 and/or liquids for subsequent release. These solids  
28 or liquids can include inhibitors such as scale  
29 inhibitors and other oilfield production chemicals  
30 for release into the wellbore of an oil or gas  
31 producing well or a water injection well.

1 The material can be used for sand control and for  
2 hydraulic fracturing (for clarity the material shall  
3 herein be termed "a proppant" when it is applied to  
4 hydraulic fractures) and well clean up. The material  
5 can be used for sand control purposes whilst also  
6 providing controlled release of oilfield production  
7 chemicals from within the sand control medium. This  
8 includes application in gravel packed, fracture  
9 packed and pre-packed screen sand control systems.  
10 The material can also be used for more effective well  
11 clean up after completion in both injection and  
12 production wells via the controlled release of enzyme  
13 based materials that release acids to dissolve any  
14 mineral deposits and breakdown residual bio-polymers  
15 from the well completion process. The material can  
16 be used for hydraulic fracturing purposes whilst also  
17 providing controlled release of oilfield production  
18 chemicals from within the proppant medium. In  
19 addition this material may be used for hydraulic  
20 fracturing and either or both the controlled release  
21 of oilfield chemicals and proppant flow back control.  
22 The material may also be used within the rathole of a  
23 well to provide controlled release of an oilfield  
24 chemical into the aqueous environment.  
25  
26 Preferably the polymeric material is used for sand  
27 control and hydraulic fracturing.  
28  
29 Preferably the polymeric material is permeable.  
30

1 The material can comprise a polymeric plastics  
2 material such as polypropylene, polyethylene, high  
3 density polyethylene, high density polypropylene,  
4 polyethylene terephthalates, polyamides (both  
5 aliphatic and aromatic), liquid crystal polymers,  
6 liquid engineered resins, starch and polyhydroxy  
7 alkanates or mixtures of these.

8  
9 The material typically comprises a matrix that  
10 provides the material with support, and which  
11 contains the chemical to be released.

12  
13 Other materials may be used as the matrix such as  
14 acrylic, polybutylene, polycarbonate, polyester,  
15 polystyrene, polyurethane, polyvinyl chloride,  
16 polycaprolactone, polybutylene terephthalate,  
17 polyvinyl alcohol, polylactic acid, polyglycolide,  
18 polyester amide, polyimides, acrylonitrile-butadiene-  
19 styrene, acrylonitrile-styrene-acrylate,  
20 polyoxymethylene, polybutylene, polyisobutylene,  
21 polyvinylbutyral, epichlorohydrin elastomer, nitrile  
22 elastomer, nitrile rubber, polyetherketone,  
23 polyetheretherketone, polyetherketoneketone,  
24 polymethylmethacrylate, polyethylene oxide,  
25 polyphenylene oxide, polysulphones,  
26 polyethersulphone, polyurea, chlorinated  
27 polyethylene, ethylene-chlorofluoroethylene,  
28 tetrafluoroethylene-perfluoropropylene,  
29 Perfluoroalkoxy, silicon rubbers and other polymeric  
30 materials consisting of mixtures of the above and  
31 copolymers, terpolymers and

1 hydrophobically/hydrophilically modified and  
2 crosslinked derivatives of the above.

3

4 Other materials can be used instead of or in addition  
5 to the polymeric or plastics material, such as  
6 thermoplastic rubber, resins, hot melt adhesives,  
7 fibreglass, silicones, fluorosilicones e.g. Ryton,  
8 polysiloxanes, fluoroelastomers e.g. Viton, Aflas,  
9 fluorocarbons e.g. PTFE, PVDF, halogenated polymers,  
10 cellulose, polysaccharides, lignin, chitin, gums and  
11 mixtures and derivatives of the above.

12

13 In addition waxes, calcium stearate, and metallocene  
14 can be used instead of or in addition to the  
15 polymeric or plastics material.

16

17 The material contains a high active content of scale  
18 inhibitor, or the chemical to be released, typically,  
19 10-90wt%/v. The high mass of inhibitor contained  
20 within the capsule can reduce (and on some wells  
21 potentially eliminate) the need for scale related  
22 intervention. In addition, the high loading of  
23 inhibitor offers the potential for significant  
24 treatment lifetime with minimal product deployment.

25

26 The release of the scale inhibitor can be further  
27 controlled by changing its solubility in the brine  
28 phase or by restricting contact between the inhibitor  
29 salt and the brine phase. The solubility of the  
30 inhibitor in the brine phase can be reduced by  
31 increasing the ratio of the polyvalent cation to

1 inhibitor in the precipitated salt or by changing the  
2 nature of the polyvalent cation. Careful selection  
3 of the polymer type or the use of hydrophobic  
4 additives can reduce water ingress into the porous  
5 matrix and thus reduce inhibitor release.

6  
7 In certain embodiments the hardness of the material  
8 can be varied by changing the chemical composition of  
9 the polymer plastic matrix and/or cross-linking the  
10 polymer plastic material or by reinforcing the  
11 particle matrix with natural, synthetic, glass or  
12 metal fibres, sand, silicates or other minerals and  
13 ceramic matrices such as bauxite, resins, carbon or  
14 boron based materials and impact modifiers. Typically  
15 the unconfined compressive strength would be in the  
16 range 500-100,000psi.

17  
18 In other embodiments the material can be selected to  
19 have an oil tolerance which can be adjusted by  
20 changing the chemical composition of the polymer  
21 plastic matrix and/or modifying the hydrophobic or  
22 hydrophilic properties of the polymer matrix or  
23 cross-linking the polymer matrix with a suitable  
24 reagent. In addition, the chemical resistance to  
25 acids and oil may be increased by the addition of a  
26 chemical stabiliser, for example Ebonite.

27  
28 The capsules are typically of permeable polymeric  
29 material, and are manufactured using an underwater  
30 pelletising system consisting of an extrusion and  
31 either a spheronisation or granulation process. The



1 capsules typically contain a high active content of  
2 scale inhibitor, typically, 10-90wt%/v. The  
3 particles can be produced over a wide range of sizes.  
4 The size distribution of the particles in a sample of  
5 material can be large, with a heterogeneous  
6 distribution of particles of different sizes, or  
7 small, with a fairly homogeneous range of similarly  
8 sized particles (so called mono dispersed particles).  
9 The range of preferred sizes is typically 250µm -  
10 5mm, with the distribution of size being typically  
11 ±5% of the mean size.  
12

13 The density of the capsules can be controlled by the  
14 variation of the type of polymer matrix and/or by  
15 including a weighting agent such as barite, zirconium  
16 oxide, manganese oxide, titanium dioxide, tungsten or  
17 magnetite. The hardness, compressive strength and  
18 elastic properties (rigidity and  
19 elongation/deformation) can be controlled by the  
20 variation of the type of polymer matrix and/or  
21 including a strengthening agent such as glass, sand,  
22 minerals, carbon or boron fibres and/or an impact  
23 modifier. The unconfined compressive strength is  
24 typically between 500-100,000psi.  
25

26 The material is typically extruded from a pelletising  
27 system. A single or twin screw system can be used,  
28 and other mixers such as Farrell and Banbury mixers  
29 or a Feeder extruder can be used.  
30

1 Mono dispersed spherical particles (i.e. a relatively  
2 homogeneous mixture of similarly sized particles) can  
3 be produced over a wide range of particle size,  
4 typically 250 $\mu$ m - 5mm, with the distribution of size  
5 being typically  $\pm 5\%$  of the mean size. The variation  
6 in particle size can allow certain embodiments of the  
7 invention to provide gravel packs of different mesh  
8 sizes, where in certain embodiments there is an  
9 advantage in having a narrow range of particle sizes  
10 in the one application. The spherical and mono  
11 dispersed nature of the particles typically provides  
12 better packing in the gravel pack and a more uniform  
13 pore throat size. This can provide more effective  
14 sand control and reduce the turbulence in the pore  
15 throats, thus improving the gravel pack permeability.

16  
17 In certain embodiments, the material can have a low  
18 and adjustable density (specific gravity usually  
19 between 0.9 and 2.0 where mostly polymeric materials  
20 are used, and even higher SG values up to 12 can be  
21 achieved with a higher proportion of heavier  
22 materials e.g. mostly tungsten) and that can be  
23 adjusted by changing the chemical composition of  
24 polymeric matrix and/or by adding a weighting agent  
25 such as barite, tungsten, zirconium oxide or  
26 magnetite or any other material denser than the  
27 polymer. The optional low density of the material  
28 can provide more effective gravel pack placement and  
29 simplify the gravel-packing operation, especially in  
30 deviated wells because the high viscosity fluids  
31 normally needed to carry dense proppant and/or gravel

1 pack material through a pipeline system will not be  
2 needed.

3

4 In certain embodiments, typically for application in  
5 rat holes, the polymer matrix can slowly degrade over  
6 a time period of 1 week to 10 years leaving little or  
7 no residue. This will typically enable re-treatment  
8 of the product into the rathole once the product has  
9 degraded. The lifetime of the plastic capsule can be  
10 adjusted by changing the chemical composition and  
11 molecular weight of the polymeric matrix and/or  
12 incorporating a dissolution agent such as heavy  
13 aromatic naphthas, peroxides, per sulphates, enzymes  
14 and metal oxide catalysts into the spherical plastic  
15 capsule. The rate and lifetime of release of the  
16 encapsulated chemical can be controlled such that it  
17 corresponds to the degradation lifetime of the  
18 polymer matrix material. This may be achieved by  
19 varying the amount of encapsulated chemical in the  
20 polymer matrix material, changing the chemical  
21 composition of the polymer matrix and the inhibitor  
22 salt or by coating the polymer matrix and/or coating  
23 the encapsulated inhibitor salt.

24

25 In certain embodiments, for application in gravel  
26 packs and hydraulic fractures, the polymeric material  
27 is preferably somewhat pliable so that it can display  
28 a slight amount of deformation at the point of  
29 contact, increasing the surface area of contact  
30 between particles. In gravel packs and hydraulic  
31 fractures this reduces the effect of applied stress

1 and can result in improved sand and proppant flowback  
2 control respectively. The amount of deformation of  
3 the polymer matrix required to control sand  
4 production and proppant flowback can be adjusted by  
5 changing the chemical composition of the matrix  
6 and/or including a strengthening agent such as glass,  
7 sand, minerals, carbon or boron fibres and/or an  
8 impact modifier. Laboratory data from stressed  
9 cyclic flow back tests with mixtures of conventional  
10 proppant and chemically impregnated conventional  
11 porous proppant had indicated that although these  
12 mixtures passed the initial conductivity tests the  
13 proppant pack collapsed under cyclic stress and  
14 flowed out of the test apparatus. However, when the  
15 same tests were repeated with mixtures of  
16 conventional proppant and this polymeric material no  
17 proppant flow back was observed. This was  
18 attributed to cohesion of the proppant pack induced  
19 by the flowback control characteristics of the  
20 polymeric material.

21  
22 Most preferred embodiments of the material comprise  
23 spherical capsules although other shapes may be in  
24 accordance with the invention. Spherical capsules  
25 have the additional advantage for gravel pack  
26 applications in that they can be packed more  
27 efficiently into a defined space than other shapes of  
28 material. In addition, the use of a more homogeneous  
29 particle size typically leads to the formation of  
30 more homogeneous pore throats. This can afford the  
31 gravel pack more effective sand control

1 characteristics and can reduce the turbulence within  
2 the sand or proppant pack, which may lead to an  
3 increased effective permeability.

4

5 In preferred embodiments of the invention the  
6 material is charged with any scale inhibitor suitable  
7 for the purpose of inhibiting scale in a well bore  
8 formation. This may include water soluble organic  
9 molecules with carboxylic acid, aspartic acid, maleic  
10 acids, sulphonic acids, phosphonic acid and phosphate  
11 esters groups including copolymers, ter-polymers,  
12 grafted copolymers and derivatives of the above.  
13 Examples of such compounds include aliphatic  
14 phosphonic acids such as diethylene triamine penta  
15 (methylene phosphonate) and polymeric species such as  
16 polyvinylsulphonate. The scale inhibitor can be in  
17 the form of the free acid but is preferably in the  
18 form of mono and polyvalent cation salts such as Na,  
19 K, Al, Fe, Ca, Mg,  $\text{NH}_4$ .

20

21 The chemicals can be solid and mixed with the matrix  
22 to give a generally homogeneous mixture comprising  
23 the plastics matrix and the chemical. Alternatively,  
24 the scale inhibitors etc can be encapsulated in  
25 liquid form e.g. by being immobilised, absorbed or  
26 encapsulated in an appropriate matrix such as a  
27 diatomised clay, resin, starch or other  
28 polysaccharide material, polyvinyl alcohol and super-  
29 adsorbing polymers and then being incorporated in  
30 solid form into the main product matrix.

31

1 The material can contain scale inhibitor in most  
2 preferred embodiments but instead in other  
3 embodiments either no chemical is included in the  
4 formulation or a wide range of other oil field  
5 chemicals such as inhibitors can be carried including  
6 but not limited to corrosion inhibitors, biocides,  
7 wax and asphaltene control chemicals, pour point  
8 suppressants, dispersants, hydrate and halite  
9 inhibitors, demulsifiers, gel breakers, tracers, drag  
10 reducers and well clean up chemicals including  
11 enzymes. These can also be encapsulated in either  
12 solid or liquid form into the material.

13  
14 Certain embodiments of the present invention tackle  
15 sand and combined sand/scale control in gravel packed  
16 and pre-packed screen wells by using a hard,  
17 permeable, spherical plastic capsule, optionally  
18 carrying a chemical substance such as an inhibitor,  
19 although other embodiments can simply provide an  
20 alternative material to sand or gravel for use in  
21 gravelpacks. The plastic capsule can be manufactured  
22 using a hot melt extrusion and spheronising process  
23 and can optionally contain approximately 10-90wt% of  
24 active scale inhibitor and can benefit from a low and  
25 adjustable density. The high mass of inhibitor  
26 contained within the particle can reduce the need for  
27 scale-related intervention and offers the potential  
28 for significant treatment lifetime. The low density  
29 of the particle also aids placement and simplifies  
30 the gravel packing operation. In addition, the  
31 spherical nature and mono dispersed characteristics

1 of the plastic capsule can provide more effective  
2 packing and a uniform pore throat size for the gravel  
3 pack. This can provide improved sand control and  
4 increase the pack permeability through reduced  
5 turbulence at pore throats. The provision of a  
6 material for sand and/or combined sand/scale control  
7 in e.g. gravel packed and pre-packed screen wells  
8 comprising a hard, optionally permeable material with  
9 or without a loading of chemical to be delivered to  
10 the well is another aspect of the present invention,  
11 typically where the material comprises a number of  
12 particles having a narrow size range e.g. 400um+/-5-  
13 10%.

14

15 The invention also provides a method of treating a  
16 well, the method comprising loading a substance into  
17 a polymeric material, inserting the material into the  
18 well, and allowing the substance to leach from the  
19 polymeric material into the well.

20

21 Typically the material is inserted into a fissure,  
22 fracture, screen area, gravel pack, fracture pack or  
23 a pre-packed screen, usually as part of the well  
24 completion.

25

26 The invention also provides a method of forming a  
27 chemical-releasing particle for release of chemicals  
28 in a fluid environment, the method comprising mixing  
29 the chemical to be released with a matrix material  
30 forming the particle, and thereafter forming the  
31 particle (e.g. by melting, mixing and/or extrusion of

1 the mixture) from the mixture of the matrix and the  
2 chemical, so that the chemical is dispersed  
3 (preferably homogeneously) throughout the formed  
4 particle.

5  
6 In an extruder system, the polymeric matrix material  
7 and the other additives are typically fed into the  
8 top of the extruder via a hopper at the rear of the  
9 extruder system. The extruder is preferably an auger  
10 type mixer, which is typically heated to melt the  
11 polymer matrix. The auger screw system then  
12 typically mixes and disperses the other additives in  
13 the molten polymer as the mixture typically moves  
14 along the auger screw. Typically a vent is provided  
15 before the material reaches the head of the extruder  
16 to allow gas or moisture to escape. However this  
17 venting can be further enhanced by fitting a vacuum  
18 pump to more effectively withdraw gas and moisture.  
19 The mixture typically proceeds into a throat which  
20 typically slows down the mixture and typically  
21 increases the pressure before typically releasing the  
22 mixture in the form of strands of typically circular  
23 cross section that are extruded through apertures in  
24 an extrusion head. The strands are then typically  
25 cooled in a water bath and typically pelletised into  
26 cylindrical pellets using a chopper. The temperature  
27 of the heated extruder screw is normally dependent on  
28 the melting point of the polymers, but the typical  
29 extrusion temperatures vary between 100°C and 400°C.

30



1 The invention also provides a polymeric downhole  
2 proppant.

3

4 The invention also provides a method of supporting a  
5 well or a portion thereof, comprising disposing a  
6 support material in the well or portion to be  
7 supported, wherein the support material comprises a  
8 polymeric material.

9

10 The invention also provides a polymeric material for  
11 use downhole for the control of particulate matter  
12 entering the production stream of the well.

13

14 The invention also provides a method of controlling  
15 the entry of particulate matter into the production  
16 stream of a well, the method comprising disposing a  
17 number of polymeric devices into the wellbore between  
18 the formation and the production fluids outlet of the  
19 well.

20

21 Examples of the present invention will now be  
22 described by way of illustration only and with  
23 reference to the accompanying figures, wherein

24

25 Fig. 1 is a schematic representation of  
26 apparatus for producing devices according to the  
27 invention;

28 Fig. 2 is a graph plotting the concentration of  
29 scale inhibitor against the number of cycles of  
30 fluid passing through a closed system;

1        Figure 3 shows the plot of compressive stress  
2        (psi) versus axial strain for certain  
3        embodiments of devices;  
4        Figure 4 shows a graph of pore throat size  
5        distribution versus gravel pack compressive  
6        stress as determined from a mercury stress  
7        injection test on a further embodiment;  
8        Fig 5 shows a thin section photomicrograph of a  
9        sand slurry injection test of a further  
10        embodiment;  
11        Fig 6 shows a graph of the % weight loss of  
12        total material and scale inhibitor versus the  
13        degradation time of the another embodiment of  
14        material in days at 107°C; and  
15        Fig 7 shows scale inhibitor release profile  
16        under simulated rathole conditions for PHA  
17        polymer in produced brine at 107°C in another  
18        embodiment.  
19  
20        To form the capsules an underwater pelletising  
21        process is used, which utilises an extruder having  
22        either a single screw or twin screw system. A single  
23        screw extruder comprises a steel tube of variable  
24        length, which has one single shaft screw that rotates  
25        at speed in the tube as it is heated, melting the  
26        polymer and mixing it as it is pushed down the tube.  
27        A twin screw extruder consists of two co-rotating  
28        screws in a single barrel with a variety of mixing  
29        zones down the length of the heated barrel in which  
30        both screws work together to mix and blend. This  
31        works the material more effectively compared with a

1 single screw extruder and a better dispersion of the  
2 solid additives into the polymer is achieved.

3

4 The dispersion of the material additives into the  
5 binder or polymer can be divided into four steps:

6

7 (a) wetting of the additives = pre-mixing of the  
8 additives with the binder;

9 (b) dispersion of agglomerates into aggregates and  
10 primary particles;

11 (c) distribution into the binder or polymer;

12 (d) stabilisation against re-agglomeration.

13

14 The plastic/chemical mix is then introduced into a  
15 known underwater pelletising system shown in Fig. 1.

16 The Fig. 1 system is suitable generally for producing  
17 pellets according to the invention.

18

19 The pre-extruded cylindrical pellets or the polymeric  
20 matrix material and additives for example inhibitors  
21 and weighting agents are fed via a hopper into an  
22 extruder or melt pumps which force the molten mixture  
23 through a screen changer and/or polymer diverter  
24 valve, which helps build up the pressure at the head,  
25 and for the start-up of the run. A gear pump can be  
26 used to regulate the flow of polymer to the head to  
27 keep the pressure evenly distributed throughout the  
28 system. The mixture then flows through a die 10  
29 having a series of holes arranged in a circular  
30 pattern. As the mixture emerges from the holes, it  
31 is cut into lengths by rotating blades 12 and is

1 solidified into pellets by process water which is  
2 pumped through conduits 15 across the material face  
3 in the cutting chamber 17. Tempered water transfers  
4 the pellets via conduits 20 to a centrifugal dryer  
5 and spheroniser 22 where the water and the pellets  
6 are separated and the dry spherical pellets are  
7 discharged via chute 25. The process water is  
8 filtered, pressurised, tempered and returned to the  
9 Cutting chamber 17. The system can produce pellets  
10 (e.g. mono dispersed pellets) typically at between 10  
11 to 6000kg/hr in a size range typically from 40µm to  
12 5mm ±5%.

13

14 The extrusion process may be combined with a Farrell  
15 bridge consisting of two mixing areas. In the first  
16 area the mixture is melted and mixed in an upper  
17 chamber using single screw, before it is dropped down  
18 to two co-rotating screws in the bottom chamber,  
19 where further mixing of the product occurs before it  
20 is delivered to the head of the chamber. A venting  
21 process takes place between the top and bottom  
22 chambers to remove any moisture. This venting  
23 process can be enhanced by use of a vacuum pump  
24 system.

25

26 A hole may be cut into the side of the extruder,  
27 usually two-thirds of the way down the barrel and it  
28 is used to feed additives and fillers directly into  
29 the barrel, commonly termed a feeder extruder.

30

1 An oil-heated drum mixer or Banbury Mixer may be used  
2 to slowly turn and blend the polymers and additives.  
3 The additives usually need to be more thermally  
4 stable and the mixing process is much slower.

5  
6 The spherical plastic capsule may have a variable oil  
7 tolerance which can be adjusted by changing the  
8 chemical composition of the polymer plastic matrix  
9 and/or modifying the hydrophobic or hydrophilic  
10 properties of the polymer plastic matrix or cross-  
11 linking the polymer plastic matrix with a suitable  
12 reagent. To modify the polymer a thermally stable  
13 hydrophobic group such as an aliphatic or an aromatic  
14 amide, lauryl or phosphate ester, or any other  
15 hydrophobic group is grafted onto the polymer  
16 backbone as a side chain. This provides the polymer  
17 with improved oil or water resistance depending on  
18 the nature of the polymer matrix and the modification  
19 process. In the cross-linking process, the polymer  
20 molecules are linked using peroxide, silanes and  
21 metallocene chemicals to form a more complex  
22 macromolecular structure. This is then cured at  
23 various temperatures to achieve improved strength and  
24 oil, water, acid and bacterial resistance.

25  
26 The scale inhibitors may be encapsulated in liquid  
27 form if they are immobilised on an appropriate matrix  
28 such as a diatomised clay, resin, super-adsorbing  
29 polymer and high porosity versions (~40-50%) of the  
30 main polymer matrix material. In the immobilisation  
31 process a liquid is incorporated into a solid matrix

1 by a spray drying, shear mixing, emulsion  
2 polymerisation, coating or by a simple soaking  
3 process in which the liquid is either imbibed into or  
4 adsorbed onto the surface of the solid material.

5  
6 Coatings can be applied to the outer surfaces of the  
7 capsules; for example, organic surfactants and waxes  
8 can be added to the polymer melt or applied to the  
9 outer surfaces of the resultant particle to achieve  
10 improved oil, water, acid and bacterial resistance.  
11 In addition, the polymer melt additive or surface  
12 coating can also be used to control the release rates  
13 of the encapsulated chemical into the wellbore of an  
14 oil or gas producer well or a water injection well.

15  
16 The resultant spherical particles may be injected  
17 into an oil well or water injection well. Certain  
18 embodiments of the particles can withstand  
19 particularly high pressures associated with such  
20 wells. The particles may be injected into the rat-  
21 hole, hydraulic fractures or into the annulus in  
22 gravel packed, fracture packed and pre-packed sand  
23 screen completed wells. The chemicals such as scale  
24 inhibitors will gradually over time leak out from the  
25 particles and so treat the local environment  
26 accordingly. The release rate can be controlled by  
27 varying the amount of encapsulated chemical in the  
28 polymer matrix material, changing the chemical  
29 composition of the polymer matrix and the inhibitor  
30 salt or by coating the polymer matrix and/or coating  
31 the encapsulated inhibitor salt.

1     Examples

2

3     **Example 1** - Extrusion Temperature 165°C - 200°C

4

5     Particles were produced using the above Fig. 1 device  
6     and having the following proportion of constituents:-

7

8     40% PP/HDPE (60/40 mix of polypropylene/high density  
9     polyethylene) - as the plastic matrix material; The  
10    material can be added as a fine powder of average  
11    size 0-100µm.

12

13    30% Magnetite (Iron oxide) - as the weighting agent;  
14    The material can be added as a fine powder with an  
15    average particle size of 1-100µm.

16

17    30% Solid Polycarboxylate - as a scale inhibitor  
18    salt. The material can optionally be added as a fine  
19    powder with an average particle size of 1-100µm, and  
20    typically around 70µm or less.

21

22    The plastic matrix material and the other two  
23    components were added into the hopper and fed into  
24    the top of the extruder. The mixture was then melted  
25    within the heated auger type mixer and the components  
26    dispersed in the polymer matrix, as described earlier  
27    in the manufacturing process, before being extruded  
28    using the underwater pelletising system also  
29    described earlier. The finished capsule was  
30    particularly suitable for rat hole applications where

1 a weighting agent is normally necessary to keep it in  
2 place and prevent it from floating out of position.  
3 The specific gravity of this material was ~1.4 and  
4 it's unconfined compressive strength was >500psi.  
5 The product was also thermally stable in both brine  
6 and oil up 140°C. However, above this temperature  
7 the product will soften and agglomerate and may break  
8 down in crude oil. The scale inhibitor was an  
9 optional constituent, and this can be omitted in  
10 embodiments intended for gravelpack applications.

11

12 **Example 2 - Extrusion Temperature 165°C - 200°C**

13

14 Particles were produced using the above Fig. 1 device  
15 and having the following proportion of constituents:-

16

17 60% PP/HDPE (60/40 mix of polypropylene/high density  
18 polyethylene) - as the plastic matrix material; The  
19 material can be added as a fine powder with an  
20 average particle size of 1-100µm.

21

22 2% Tungsten - as the weighting agent; The material  
23 can be added as a fine powder with an average  
24 particle size of 1-100µm.

25

26 38% Solid Polycarboxylate. The material can be added  
27 as a fine powder with an average particle size of 1-  
28 100µm.

29

30 This capsule was manufactured as detailed for the  
31 previous example. The product is typically suitable



1 for scale control in rat holes. The reduction in the  
2 amount of weighting agent in the plastic capsule  
3 optionally allows more scale inhibitor to be loaded  
4 into the product agent, thus potentially increasing  
5 the treatment lifetime. The reduction in the amount  
6 of weighting agent also increases the compressive  
7 strength. The specific gravity of this material was  
8 ~1.20 and its unconfined compressive strength was  
9 greater than 1000psi. The product displayed a  
10 thermal stability similar to that in Example 1.  
11 Again, the scale inhibitor was an optional  
12 constituent, and this can be omitted in embodiments  
13 intended for gravelpack applications.  
14

15 **Example 3 - Extrusion Temperature 200-220°C**  
16

17 Particles were produced as described for the previous  
18 2 examples and having the following proportion of  
19 constituents:-  
20

21 50% PP/HDPE (60/40 mix of polypropylene/high density  
22 polyethylene) - as the plastic matrix material. The  
23 material can be added as a fine powder with an  
24 average particle size of 1-100µm  
25

26 30% Glass - Strengthening Agent. The material can be  
27 added as a fine powder with an average particle size  
28 of 1-100µm.  
29

30 20% Solid THPS (Tetrakis(hydroxymethyl)phosphonium

1 sulphate) - as a biocide salt. The material can be  
2 added as an agglomerate with an average particle size  
3 of 50-2000 $\mu$ m.  
4

5 This capsule was manufactured as detailed for the  
6 previous example. The extrusion temperature was  
7 slighter higher to ensure the glass which was added  
8 as a fine powder was properly dispersed during the  
9 extrusion process. The addition of glass strengthens  
10 the capsule by up to 10% as well as increasing the  
11 oil resistance and thermal stability of the product  
12 to over 150°C. The specific gravity of this material  
13 was ~1.20. The unconfined compressive strength was  
14 1100psi. This capsule can be used for the control of  
15 sulphate reducing bacteria to prevent the generation  
16 of H<sub>2</sub>S and associated corrosion problems.  
17

18 **Example 4 - Extrusion Temperature 200°C - 240°C**  
19

20 Particles were produced as described above for the  
21 previous three examples and having the following  
22 proportion of constituents:  
23

24 80% PET/PP (20/80 mix of polyethylene  
25 terephthalate[PET)/polypropylene[PP]) - as the  
26 plastic matrix material; the material can be added  
27 as a fine powder with an average particle size of 1-  
28 100 $\mu$ m.  
29

1     20% Solid Phosphonate - as a scale inhibitor salt.  
2     The material can be added as a fine powder with an  
3     average particle size of 1-100 $\mu$ m.  
4

5     This capsule was manufactured as detailed for the  
6     previous two examples. The inclusion of polyethylene  
7     terephthalate in the main matrix material  
8     strengthened the bead by a factor of 3 and can be  
9     suitable for applications that require the capsule to  
10    withstand high pressures. In addition, the inclusion  
11    of PET imparts more oil resistance and increase the  
12    thermal stability of the product to >180°C. The  
13    specific gravity of the material was ~1.3 and it's  
14    unconfined compressive strength was >3400psi.  
15

16    **Example 5** - Extrusion Temperature 200 - 260°C  
17

18    This capsule was manufactured as detailed for the  
19    previous two examples and having 100% Polyamide  
20    (Nylon) as the plastic material.  
21

22    The use of polyamide as the main matrix material  
23    provided even more strength than the bead as quoted  
24    in Example 4. The compressive strength was again  
25    increased by a factor of 3 and use of Polyamide  
26    increases the chemical resistance and thermal  
27    stability of the product to >250°C. The material can  
28    be suitable for sand control in applications that  
29    require the plastic capsule to withstand extremely  
30    high pressures and, in addition, the polyamide matrix  
31    material can display a slight amount of deformation

1 and can be used for proppant flowback control in  
2 hydraulic fractures and gravel packs. Typically this  
3 embodiment excludes any substance to be released from  
4 the capsule, but can incorporate such substances if  
5 desired.

6  
7 The specific gravity of this material was ~1.2-1.3  
8 and its unconfined compressive strength exceeded  
9 12000psi.

10

11 **Example 6 - Extrusion Temperature 200°C -260°C**

12

13 This capsule was manufactured as detailed for the  
14 previous two examples and has the following  
15 proportion of constituents:

16

17 70% Polyamide - as the plastic matrix material. The  
18 material can be added as a fine powder with an  
19 average particle size of 1-100µm.

20

21 30% Solid Phosphonate - as a scale inhibitor salt.  
22 The material can be added as a fine powder with an  
23 average particle size of 1-100µm.

24

25 This capsule can be used for sand and proppant flow  
26 back control and combined sand/proppant flow back and  
27 scale control in gravel packs, fracture packs, screen  
28 wells and hydraulic fractures.

29

30 Fig. 2 shows the concentration of scale inhibitor  
31 released versus the number of pore volumes of fluid

1 eluted through the packed material. One pore volume  
2 is defined here as approximately 25% of the total  
3 volume of the packed material and corresponds to the  
4 volume in the system that is not occupied by the  
5 plastic material. It can be seen from Fig. 2 that  
6 the release of scale inhibitor is constant even after  
7 6000 pore volumes. Therefore, the scale inhibitor is  
8 released at a constant low level for long periods of  
9 time.

10

11 It can be seen from Fig. 3 that the material in  
12 Example 5 does become slightly strained as the stress  
13 is increased to > 8000-10000psi. Therefore a slight  
14 amount of deformation of the material does occur in  
15 both the presence and absence of scale inhibitor.

16

17 The specific gravity of this material was ~ 1.3 and  
18 its unconfined compressive strength was greater than  
19 10,500psi.

20

21 **Example 7 - Extrusion Temperature 165°C**

22

23 This capsule was manufactured as detailed for the  
24 previous two examples and having the following  
25 proportion of constituents:-

26

27 40% HDPE (high-density polyethylene) - as the plastic  
28 matrix material. The material can be added as a fine  
29 powder with an average particle size of 1-100µm.

30

1 30% Barite (barium sulphate) - as the weighting  
2 agent. The material can be added as a fine powder  
3 with an average particle size of 1-500µm.

4

5 30% solid polycarboxylate - as a scale inhibitor  
6 salt. The material can be added as a fine powder with  
7 an average particle size of 1-100µm.

8

9 The specific gravity of this material was ~1.3 and  
10 its compressive strength was >600psi. The product was  
11 also thermally stable in both brine and oil up to  
12 between 140°C. The finished capsule is particularly  
13 suitable for scale control in rat hole applications.

14

15 **Example 8 - Extrusion Temperature 165°C**

16

17 This capsule was manufactured as detailed for the  
18 previous two examples and having the following  
19 proportion of constituents:-

20

21 40% HDPE (high-density polyethylene) - as the plastic  
22 matrix material. The material can be added as a fine  
23 powder with an average particle size of 1-100µm.

24

25 30% Rutile (titanium dioxide) - as the weighting  
26 agent. The material can be added as a fine powder  
27 with an average particle size of 1-500µm.

28

1 30% solid polycarboxylate - as a scale inhibitor  
2 salt. The material can be added as a fine powder  
3 with an average particle size of 1-100µm.  
4

5 The specific gravity of this material was ~1.3 and  
6 its compressive strength was >1000psi. The product  
7 displayed similar thermally stability to material in  
8 example 7. The finished capsule is particularly  
9 suitable for scale control in rat hole applications.  
10

11 **Example 9 - Extrusion Temperature 200°C -260°C**  
12

13 This capsule was manufactured as detailed for the  
14 previous two examples and having the following  
15 proportion of constituents:-  
16

17 65% Polyamide/HDPE (74/16 mix of polyamide/high  
18 density polyethylene) - as the plastic matrix  
19 material; The material can be added as a fine powder  
20 with an average particle size of 1-100µm.  
21

22 28% Solid Phosphonate - as a scale inhibitor salt.  
23 The material can be added as a fine powder with an  
24 average particle size of 1-100µm.  
25

26 2% lauric diethanol amine - as an anti static agent.  
27 This material can either be added as a liquid or as a  
28 fine powder with an average particle size of 1-100µm.  
29

1     5% Calcium Stearate - as a lubricant. The material  
2     can be added as a fine powder with an average  
3     particle size of 1-100 $\mu$ m.

4  
5     This capsule can be used for sand and proppant flow  
6     back control and combined sand/proppant flow back and  
7     scale control in gravel packs, fracture packs, screen  
8     wells and hydraulic fractures.

9  
10    Figure 4 shows the pore throat size distribution  
11    versus the gravel pack compressive stress as  
12    determined from a mercury stress injection test (as  
13    documented in SPE 8294. It can be seen from Fig. 4  
14    that the pore throat size distribution is reduced  
15    exponentially with increasing compressive stress,  
16    with significant deformation occurring at >3000psi,  
17    namely, an 87% reduction in pore throat size and a  
18    substantial reduction in permeability to air. The  
19    data indicates that at a typical gravel pack  
20    compressive stress of 2000psi the product  
21    demonstrated acceptable strength characteristics.

22  
23    This material can be manufactured down to 500  $\pm$  25 $\mu$ m.  
24    The specific gravity of this material is ~1.2 and  
25    it's confined compressive strength was >2000psi.

26  
27    **Example 10** - Extrusion Temperature 165°C - 200°C.

28  
29    This capsule was manufactured as detailed for the  
30    previous two examples and having the following  
31    proportion of constituents:-



1     65% HDPE - as the plastic matrix material; The  
2     material can be added as a fine powder with an  
3     average particle size of 1-100 $\mu$ m.

4

5     30% Solid Phosphonate - as a scale inhibitor salt.  
6     The material can be added as a fine powder with an  
7     average particle size of 1-50 $\mu$ m.

8

9     2% lauric diethanol amine - as an anti static agent.  
10    This material can be added as a liquid or as a fine  
11    powder with an average particle size of 1-100 $\mu$ m.

12

13    3% wax - as a lubricant. This material can be added  
14    as a molten liquid or as a fine powder with an  
15    average particle size of 1-100 $\mu$ m.

16

17    Figure 5 shows a photomicrograph of a thin section of  
18    a gravel pack of the above 300 $\mu$ m material taken from  
19    a sand slurry injection test. The sand material was  
20    injected as a 1wt%/v slurry at 50ml/minute and the  
21    average diameter (D50) of the sand particles was  
22    100 $\mu$ m. It can be seen from Fig. 5 that none of  
23    injected sand passed into or out of the 300 $\mu$ m gravel  
24    pack material. Therefore the above material provided  
25    effective sand control at 300 $\mu$ m.

1 This material can be manufactured down to  $300 \pm 15\mu\text{m}$ .  
2 The specific gravity of this material is  $\sim 1.2$  and it  
3 is thermally stable in both oil and brine to  $>140^\circ\text{C}$ .

4

5 **Example 11** - Extrusion Temperature  $180^\circ\text{C}$  -  $220^\circ\text{C}$ .

6

7 This capsule was manufactured as detailed for the  
8 previous two examples and having the following  
9 proportion of constituents:-

10

11 70% PolyHydroxyAlkanoate (PHA) - as the degradable  
12 polymer matrix material. This material can be added  
13 as an agglomerate with an average granule size of 1-3  
14 mm.

15

16 30% solid phosphonate - as a scale inhibitor salt.  
17 This material can be added as a fine powder with an  
18 average particle size of 1- $100\mu\text{m}$ .

19

20 The finished capsule is particularly suitable for  
21 scale control in rat hole applications. The material  
22 has been designed to degrade or slowly dissolve so  
23 that it is possible to re-treat the rat hole without  
24 the need for expensive remedial cleaning procedures.

25

26 Fig. 6 shows the % weight loss of the total material  
27 and scale inhibitor versus the degradation time in  
28 days at  $107^\circ\text{C}$ . It can be seen from Fig. 6 that the  
29 material has undergone a substantial total weight  
30 loss. A comparison of the total weight loss with the  
31 % mass loss profile due to the release of the

1 encapsulated scale inhibitor, which is relatively  
2 constant at a low level, indicated that  
3 degradation/dissolution of the polymer matrix was  
4 occurring. The trends in the data indicate a  
5 predicted degradation lifetime of between 12-14  
6 months at 107°C.

7  
8 Figure 7 shows the concentration of scale inhibitor  
9 released versus the number of cell volumes of brine  
10 eluted at 107°C. The test was performed in a  
11 specially designed cell to simulate the release of  
12 scale inhibitor from a product placed in the rat  
13 hole. It can be seen from Fig. 7 that the PHA  
14 polymer matrix displays favourable scale inhibitor  
15 release characteristics, with the scale inhibitor  
16 being released at low levels over a long period.

17  
18 The specific gravity of this material was ~1.2-1.3  
19 and its compressive strength was >1000psi. The  
20 product was also thermally stable in both brine and  
21 oil up to between 170-180°C.

22  
23 **Example 12 - Extrusion Temperature 200-220°C**

24  
25 This capsule was manufactured as detailed for the  
26 previous two examples and having the following  
27 proportion of constituents:-

28  
29 61% polyethylene terephthalate (PET) - as the polymer  
30 matrix material. This material can be added as a fine  
31 powder with an average particle size of 1-100µm.

1 30% solid phosphonate - as a scale inhibitor salt.  
2 This material can be added as a fine powder with an  
3 average particle size of 1-100µm.

4

5 9% titanium oxide oxidation catalyst - as a  
6 degradation additive. This material can be added as  
7 a fine powder with an average particle size of 1-  
8 100µm.

9

10 The finished capsule is particularly suitable for  
11 scale control in rat hole applications. The material  
12 has been designed to degrade or slowly dissolve over  
13 10-14 months.

14

15 **Example 13** - Extrusion Temperature 165-200°C

16

17 This capsule was manufactured as detailed for the  
18 previous two examples and having the following  
19 proportion of constituents:-

20

21 55% starch - as the polymer matrix material. This  
22 material can be added as a fine powder with an  
23 average particle size of 1-100µm.

24

25 35% solid potassium hexacyanoferrate III - as a  
26 halite inhibitor salt. This material can be added as  
27 a fine powder with an average particle size of 50-  
28 500µm.

29

1 10% Tungsten polyamide blend- as a weighting agent.  
2 This material can be added as a granule in  
3 masterbatch format with an average granule size of  
4 500-3000 $\mu$ m.  
5

6 The finished capsule is particularly suitable for  
7 halite scale control in rat hole applications. The  
8 specific gravity of this material was -1.1-1.3 and  
9 the material is thermally stable up to 140°C:  
10

11 **Example 14** - Extrusion Temperature 165-200°C  
12

13 This capsule was manufactured as detailed for the  
14 previous two examples and having the following  
15 proportion of constituents:-  
16

17 70% polyamide - as the polymer matrix material. This  
18 material can be added as a fine powder with an  
19 average particle size of 1-100 $\mu$ m.  
20

21 30% solid enzyme - as the acid generating enzyme.  
22 This material can be added as a granule with an  
23 average particle size of 100-1000 $\mu$ m.  
24

25 This material is suitable for sand control and  
26 improved well clean up after completion in both  
27 injection and production wells.  
28

29 Modifications and improvements may be incorporated  
30 without departing from the scope of the invention.

1     Claims

2

3     1.    A substance release device comprising a  
4           polymeric material for releasing a substance  
5           into a downhole fluid environment in a well.

6

7     2.    A device according to claim 1, wherein the  
8           substance comprises one or more selected from  
9           the group comprising scale inhibitors, hydrate  
10          and halite inhibitors, corrosion inhibitors,  
11          biocides, wax and asphaltene control substances,  
12          demulsifiers, gel breakers, tracers, drag  
13          reducers and well clean up substances including  
14          enzymes; organic molecules, acids, esters, and  
15          aliphatic substances.

16

17    3.    A device as claimed in any preceding claim  
18          wherein the polymeric material is permeable.

19

20    4.    A device as claimed in any preceding claim,  
21          wherein the material is one or more selected  
22          from the group comprising polypropylene,  
23          polyethylene, high density polyethylene, high  
24          density polypropylene, polyethylene  
25          terephthalates, polyamides (both aliphatic and  
26          aromatic), liquid crystal polymers, liquid  
27          engineered resins, starch and polyhydroxy  
28          alkanoates or mixtures of these.

29

30    5.    A device as claimed in any preceding claim,  
31          wherein the material comprises a matrix that

1 provides the material with structural support,  
2 and which contains the substance to be released.

3  
4 6. A device as claimed in claim 5, wherein the  
5 material also contains one or more of the group  
6 of substances comprising acrylic, polybutylene,  
7 polycarbonate, polyester, polystyrene,  
8 polyurethane, polyvinyl chloride,  
9 polycaprolactone, polybutylene terephthalate,  
10 polyvinyl alcohol, polylactic acid,  
11 polyglycolide, polyester amide, polyimides,  
12 acrylonitrile-butadiene-styrene, acrylonitrile-  
13 styrene-acrylate, polyoxymethylene,  
14 polybutylene, polyisobutylene, polyvinylbutyral,  
15 epichlorohydrin elastomer, nitrile elastomer,  
16 nitrile rubber, polyetherketone,  
17 polyetheretherketone, polyetherketoneketone,  
18 polymethylmethacrylate, polyethylene oxide,  
19 polyphenylene oxide, polysulphones,  
20 polyethersulphone, polyurea, chlorinated  
21 polyethylene, ethylene-chlorofluoroethylene,  
22 tetrafluoroethylene-perfluoropropylene,  
23 Perfluoroalkoxy, silicon rubbers and other  
24 polymeric materials consisting of mixtures of  
25 these, copolymers, terpolymers and  
26 hydrophobically/hydrophilically modified and  
27 crosslinked derivatives of these.

28  
29 7. A device as claimed in any preceding claim,  
30 wherein the material contains one or more of the  
31 group of substances comprising waxes, calcium

- 1        stearate, metallocene, thermoplastic rubber,  
2        resins, hot melt adhesives, fibreglass,  
3        silicones, fluorosilicones e.g. Ryton,  
4        polysiloxanes, fluoroelastomers e.g. Viton,  
5        Aflas, fluorocarbons e.g. PTFE, PVDF,  
6        halogenated polymers, cellulose,  
7        polysaccharides, lignin, chitin, gums and  
8        mixtures and derivatives of the above.  
9
- 10      8.    A device as claimed in any preceding claim,  
11        comprising a generally spherical capsule.  
12
- 13      9.    A device as claimed in any preceding claim,  
14        manufactured using an underwater pelletising  
15        system using an extrusion and either a  
16        spheronisation or granulation process.  
17
- 18      10.   A device as claimed in any preceding claim,  
19        wherein the material contains a high active  
20        content of substance to be released.  
21
- 22      11.   A device as claimed in any preceding claim,  
23        including a weighting agent to adjust the  
24        density of device.  
25
- 26      12.   A device as claimed in claim 11, wherein the  
27        weighting agent is selected from the group  
28        comprising barite, zirconium oxide, manganese  
29        oxide, titanium dioxide, tungsten and magnetite.  
30



- 1     13. A device as claimed in any preceding claim,  
2         including a strengthening agent to adjust the  
3         hardness, compressive strength and/or elastic  
4         properties of the device.  
5
- 6     14. A device as claimed in claim 13, wherein the  
7         strengthening agent is selected from the group  
8         comprising glass, sand, minerals, carbon fibres,  
9         boron fibres and impact modifiers.  
10
- 11    15. A device as claimed in any preceding claim,  
12         wherein the material has a specific gravity  
13         between 0.9 and 2.0.  
14
- 15    16. A device as claimed in any one of claims 1-14,  
16         wherein the device has a specific gravity up to  
17         12.  
18
- 19    17. A device as claimed in any preceding claim,  
20         wherein the device and/or the material is  
21         pliable.  
22
- 23    18. A method of treating a well, the method  
24         comprising loading a substance into a polymeric  
25         material, inserting the material into the well,  
26         and allowing the substance to leach from the  
27         polymeric material into the well.  
28
- 29    19. A method as claimed in claim 18, wherein the  
30         substance comprises one or more selected from  
31         the group comprising scale inhibitors, corrosion

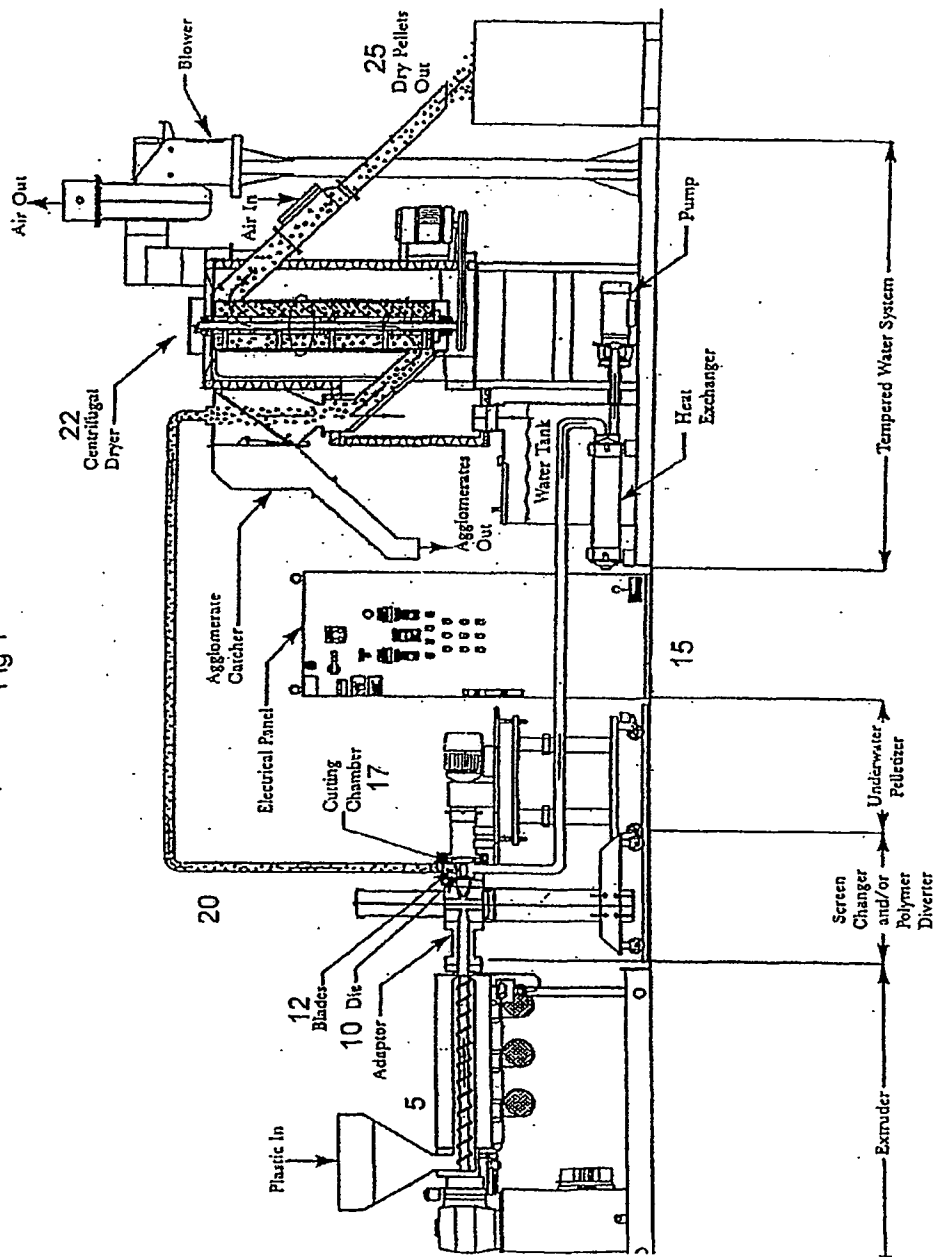
- 1 inhibitors, hydrate and halite inhibitors,  
2 biocides, wax and asphaltene control substances,  
3 demulsifiers, gel breakers, tracers, drag  
4 reducers and well clean up substances, enzymes,  
5 organic molecules, acids, esters, copolymers,  
6 ter-polymers, aliphatic compounds, polymeric  
7 species, and other oilfield production  
8 chemicals.  
9
- 10 20. A method according to claim 18 or claim 19,  
11 wherein the material releases well cleanup  
12 substances.  
13
- 14 21. A method as claimed in any one of claims 18-20,  
15 wherein the material is inserted into a fissure,  
16 fracture, screen area, gravel pack, fracture  
17 pack or a pre-packed screen.  
18
- 19 22. A method as claimed in any one of claims 18-21,  
20 wherein the material is injected into the  
21 rathole or base of a well.  
22
- 23 23. A method as claimed in any one of claims 18-22,  
24 wherein the material is used to support portions  
25 of the well, reservoir or formation in addition  
26 to releasing the substance.  
27
- 28 24. A method according to any one of claims 18-23,  
29 wherein the material controls entry of  
30 particulate matter into the production stream of  
31 the well.

- 1     25.   A method as claimed in any one of claims 18-24,  
2           wherein the material is loaded with a high  
3           active content of the substance to be released.  
4
- 5     26.   A method as claimed in any one of claims 18-25,  
6           wherein the solubility of the substance is  
7           selected to suit prevailing well conditions..  
8
- 9     27.   A method as claimed in any one of claims 18-26,  
10          wherein the hardness of the material is adjusted  
11          to suit prevailing well conditions.  
12
- 13    28.   A method as claimed in any one of claims 18-27,  
14          wherein the oil and/or acid tolerance of the  
15          material is adjusted to suit prevailing well  
16          conditions.  
17
- 18    29.   A method as claimed in any one of claims 18-28,  
19          wherein a number of the devices having a  
20          generally heterogeneous size distribution are  
21          delivered to the well.  
22
- 23    30.   A method as claimed in any one of claims 18-28,  
24          wherein a number of the devices having a  
25          generally homogeneous size distribution are  
26          delivered to the well.  
27
- 28    31.   A method as claimed in claim 30, wherein the  
29          size distribution of devices delivered to the  
30          well is  $\pm 5\%$  of the mean size.  
31

- 1     32. A method as claimed in any one of claims 29-31,  
2         wherein the range of sizes of the devices  
3         delivered to the well is 250 $\mu$ m - 5mm.  
4
- 5     33. A method as claimed in any one of claims 18-32,  
6         wherein the material is adapted to degrade over  
7         a period of time, after which the well is re-  
8         treated.  
9
- 10    34. A method as claimed in claim 33, wherein the  
11         period of degradation is adjusted to suit the  
12         prevailing well conditions.  
13
- 14    35. A method as claimed in any one of claims 18-34,  
15         wherein the rate and lifetime of release of the  
16         substance is adjusted to suit the degradation  
17         lifetime of the material.  
18
- 19    36. A method as claimed in any one of claims 18-35,  
20         wherein the material is charged with one or more  
21         substances selected from the group comprising  
22         scale inhibitors, hydrate and halite inhibitors,  
23         corrosion inhibitors, biocides, wax and  
24         asphaltene control substances, demulsifiers, gel  
25         breakers, tracers, drag reducers and well clean  
26         up substances including enzymes; organic  
27         molecules, acids, esters, and aliphatic  
28         substances.  
29
- 30    37. A method of forming a substance-releasing  
31         particle for release of substances into a fluid

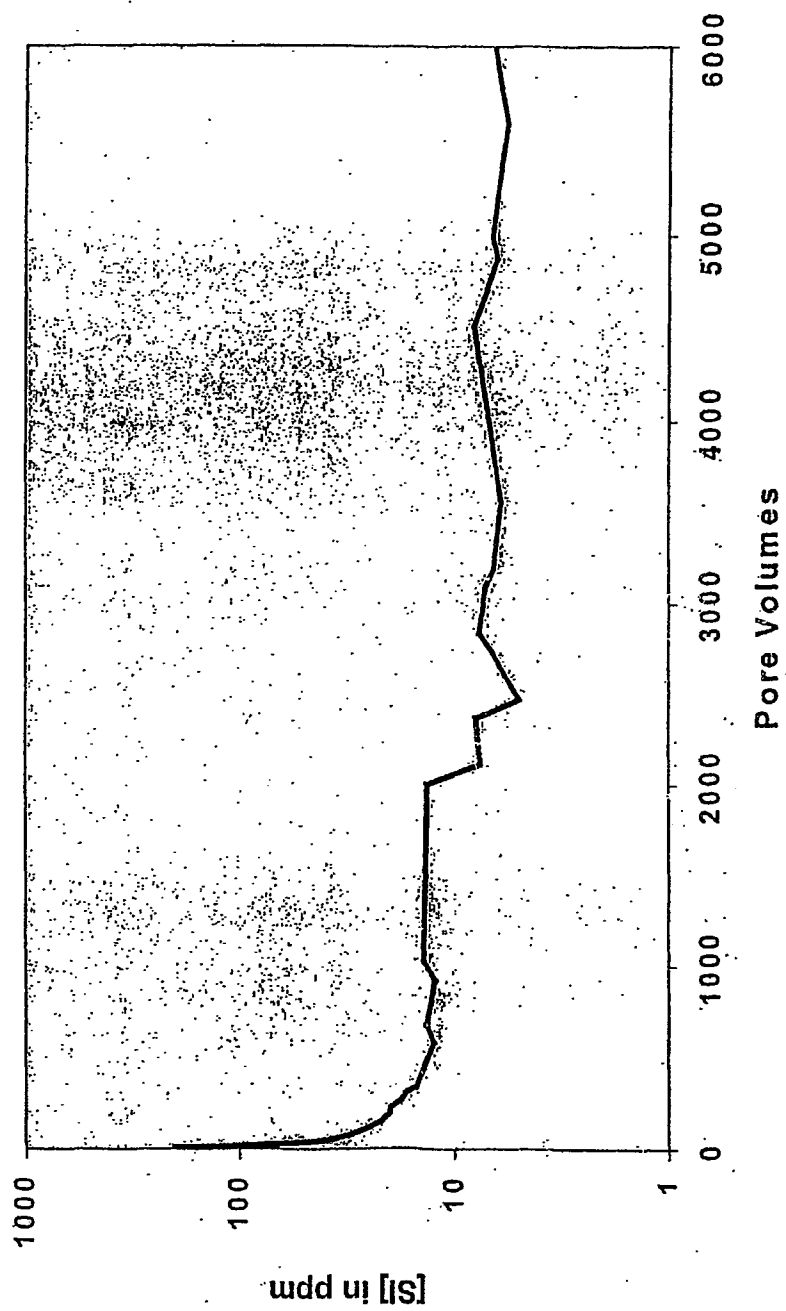
- 1 environment in an well, the method comprising  
2 mixing the substance to be released with a  
3 matrix material forming the particle, and  
4 thereafter forming the particle from the mixture  
5 of the matrix and the substance, so that the  
6 substance is dispersed throughout the formed  
7 particle.  
8
- 9 38. A polymeric downhole proppant.  
10
- 11 39. A method of supporting a well or a portion  
12 thereof, comprising disposing a support material  
13 in the well or portion to be supported, wherein  
14 the support material comprises a polymeric  
15 material.  
16
- 17 40. A polymeric material for use downhole for the  
18 control of particulate matter entering the  
19 production stream of the well.  
20
- 21 41. A method of controlling the entry of particulate  
22 matter into the production stream of a well, the  
23 method comprising disposing a number of  
24 polymeric devices into the wellbore between the  
25 formation and the production fluids outlet of  
26 the well.

Fig 1



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Fig 2 – Scale Inhibitor Release Profile from a Plastic Capsule



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Fig 3

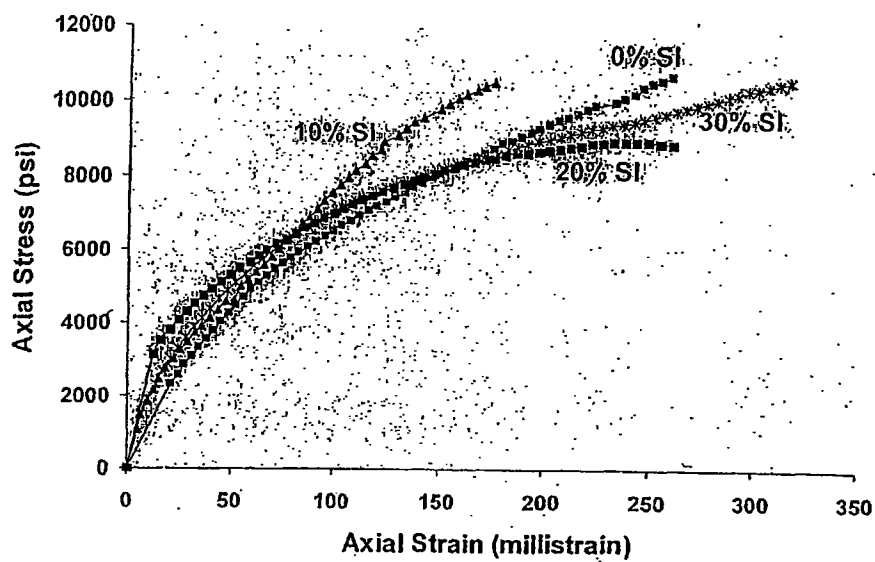
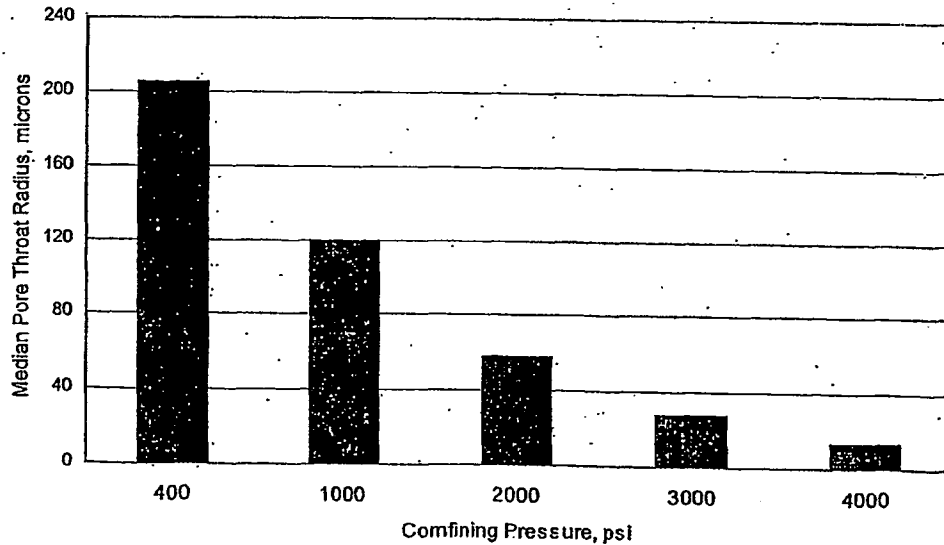


Fig 4





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Fig 5

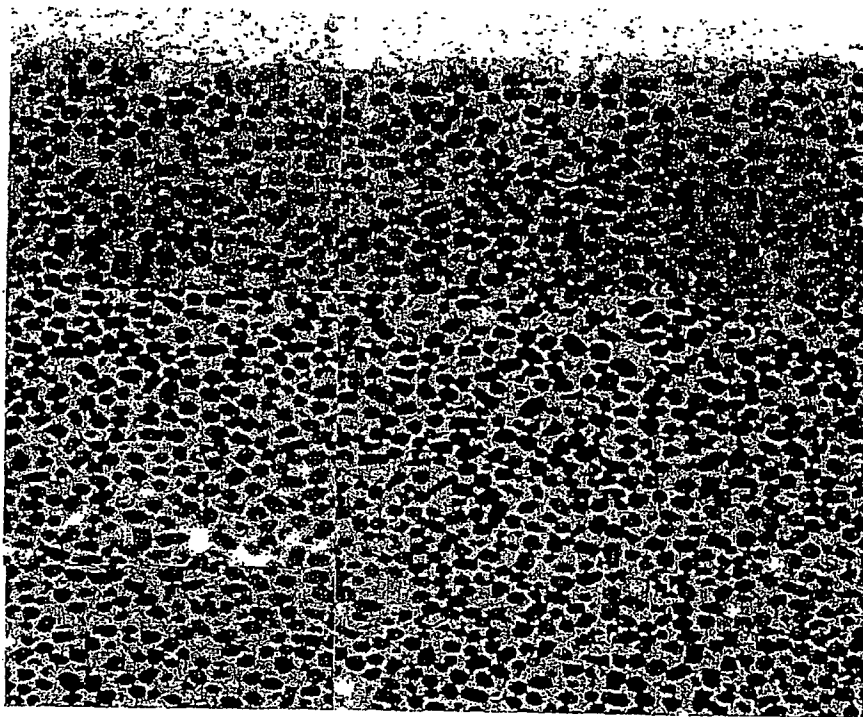
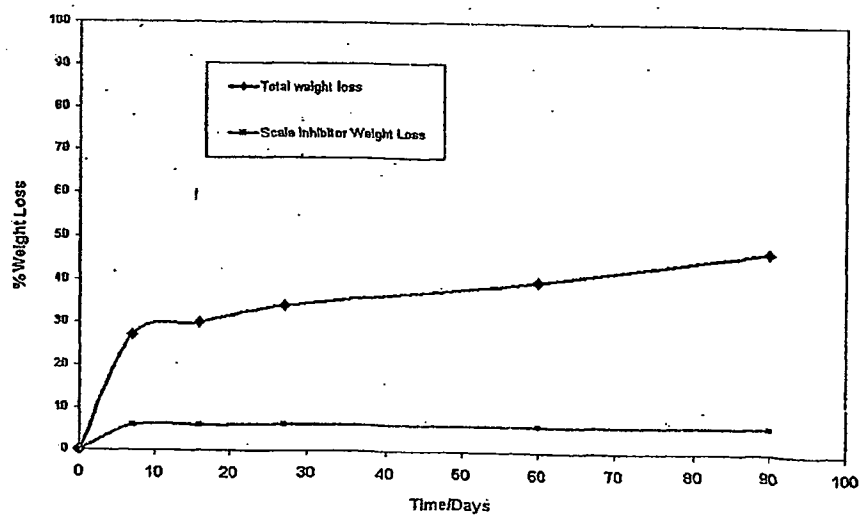
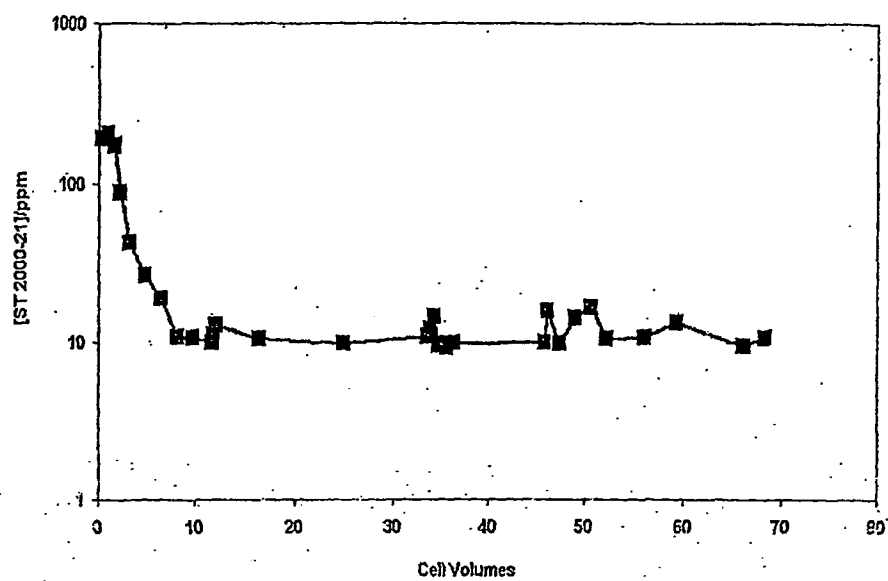


Fig 6



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Fig 7



## INTERNATIONAL SEARCH REPORT

Int lional Application No

PCT/GB 01/02482

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 E21B37/06 E21B43/25 E21B41/02 E21B43/267

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 E21B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 738 897 A (MCDUGALL ET AL.) 19 April 1988 (1988-04-19)  column 2, line 50 - column 3, line 2 column 8, line 13 - line 19 column 8, line 40 - line 44 column 9, line 1 - line 5	1-3, 5, 18, 19, 21, 33, 36, 37
X	US 3 659 651 A (GRAHAM) 2 May 1972 (1972-05-02) column 1, line 66 - column 2, line 12  --/--	38-41

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

27 September 2001

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## INTERNATIONAL SEARCH REPORT

Int lional Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 059 034 A (RICKARDS ET AL.) 9 May 2000 (2000-05-09) column 14, line 1 - line 24 column 17, line 10 - line 32 column 18, line 21 - line 24 column 20, line 57 - column 21, line 3	39-41
A	----- US 5 922 652 A (KOWALSKI ET AL.) 13 July 1999 (1999-07-13)  column 3, line 38 - line 43 column 5, line 13 - line 33 column 7, line 11 - line 35	17,23  1,2,5, 10-12, 18,19
X	US 4 986 354 A (CANTU) 22 January 1991 (1991-01-22) claim 1	1,18
X	US 4 741 401 A (WALLES ET AL.) 3 May 1988 (1988-05-03) claims 15,29	1,2,20
A	EP 0 919 695 A (FRACMASTER LTD.) 2 June 1999 (1999-06-02) page 4, line 15 - line 16	3
A	US 5 893 416 A (READ) 13 April 1999 (1999-04-13) column 2, line 19 - line 36	5,13,14
A	US 3 676 363 A (MOSIER) 11 July 1972 (1972-07-11) column 2, line 9 - line 14 column 2, line 72 - line 75 column 3, line 60 - line 72 column 6, line 17 - line 27 column 6, line 52 - line 72	8,11,22, 24,33-36
X,P	US 6 207 620 B1 (GONZALEZ ET AL.) 27 March 2001 (2001-03-27)  column 5, line 50 - column 6, line 4 column 7, line 7 - line 30 column 7, line 43 - line 45 claim 1	1,2,6,7, 9,10,18, 19,21, 25,27-32

INTERNATIONAL SEARCH REPORT  
Information on patent family members

Int lonal Application No  
PCT/GB 01/02482

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4738897	A	19-04-1988	US 4670166 A AU 583095 B2 AU 5409286 A CA 1262507 A1 DE 3673190 D1 EP 0193369 A2 NO 860713 A ,B,	02-06-1987 20-04-1989 04-09-1986 31-10-1989 13-09-1990 03-09-1986 28-08-1986
US 3659651	A	02-05-1972	NONE	
US 6059034	A	09-05-2000	AU 7600198 A GB 2348907 A WO 9927229 A1 DK 133397 A GB 2359316 A GB 2319796 A ,B NL 1007616 C2 NL 1007616 A1 NO 975440 A	15-06-1999 18-10-2000 03-06-1999 28-05-1998 22-08-2001 03-06-1998 18-01-2000 28-05-1998 28-05-1998
US 5922652	A	13-07-1999	AT 149237 T AU 4227493 A BR 9306321 A CA 2134980 A1 CZ 9402703 A3 DE 69308297 D1 EP 0639240 A1 FI 945196 A HU 70884 A2 JP 7506408 T NO 944206 A NZ 252502 A RU 2111049 C1 SK 132294 A3 WO 9322537 A1	15-03-1997 29-11-1993 26-03-1996 11-11-1993 14-06-1995 03-04-1997 22-02-1995 04-11-1994 28-11-1995 13-07-1995 04-11-1994 29-01-1997 20-05-1998 11-07-1995 11-11-1993
US 4986354	A	22-01-1991	NONE	
US 4741401	A	03-05-1988	AU 582320 B2 AU 1023188 A BR 8800186 A CA 1274767 A1 CN 88100379 A ,B GB 2199872 A ,B IN 170553 A1 MX 172677 B NO 177199 B	16-03-1989 25-08-1988 30-08-1988 02-10-1990 02-11-1988 20-07-1988 11-04-1992 07-01-1994 24-04-1995
EP 919695	A	02-06-1999	AU 9410098 A EP 0919695 A2 NO 985482 A US 6184184 B1	17-06-1999 02-06-1999 26-05-1999 06-02-2001
US 5893416	A	13-04-1999	DE 69426970 D1 DE 69426970 T2 DK 656459 T3 EP 0656459 A1 GB 2284223 A ,B	03-05-2001 13-09-2001 18-06-2001 07-06-1995 31-05-1995

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International Application No  
PCT/GB 01/02482

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5893416	A		JP 7197764 A NO 944512 A	01-08-1995 29-05-1995
US 3676363	A	11-07-1972	NONE	
US 6207620	B1	27-03-2001	AU 5455200 A WO 0075486 A1	28-12-2000 14-12-2000